Bulk Cr tips for scanning tunneling microscopy and spin-polarized scanning tunneling microscopy

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A simple, reliable method for preparation of bulk Cr tips for Scanning Tunneling Microscopy (STM) is proposed and its potentialities in performing high-quality and high-resolution STM and Spin Polarized-STM (SP-STM) are investigated. Cr tips show atomic resolution on ordered surfaces. Contrary to what happens with conventional W tips, rest atoms of the Si(111)-7×7 reconstruction can be routinely observed, probably due to a different electronic structure of the tip apex. SP-STM measurements of the Cr(001) surface showing magnetic contrast are reported. Our results reveal that the peculiar properties of these tips can be suited in a number of STM experimental situations.

Scanning tunneling microscopy (STM) is widely exploited to study surfaces with atomic resolution. Starting from its invention, it has been performed using tunneling tips fabricated with a great variety of materials. So far, the most commonly adopted tips are prepared by electrochemical etching of W wires [1]. For some specific applications, however, other materials are required. For example, in Spin Polarized STM (SP-STM) measurements, ferromagnetic or anti-ferromagnetic tips exhibiting an intrinsic spin polarization have to be used. Usual ferromagnetic tips are made of Fe[2], Ni [3], Co [4] or Fe coated W tips [5], while anti-ferromagnetic tips have been prepared using MnNi [6], MnPt [7], Cr [8, 9, 10], Cr-coated [11] or Mn-coated [12] W tips . Anti-ferromagnetic materials are usually preferred because they do not exhibit significant perturbing stray field and are not influenced by external fields. Cr is the only metal with a (bulk) Néel temperature (311 K) above room temperature (RT) and this makes it interesting in non cryogenic SP-STM. MnNi and MnPt alloys have a higher Néel temperature but, usually, tips obtained by etching are characterized by a lack of stoichiometry that could produce a net magnetization of the apex. These considerations motivate the aim of this work, which consists in the development of a simple preparation method of bulk Cr tips and in a first investigation of their properties as STM and SP-STM probes.

Previous results concerning the preparation and use of bulk Cr tips for STM are reported in Refs. 8, 9, 10. In particular, in Refs. 8, 9 Cr tips have been prepared by etching of Cr rods in KOH solution and subsequent mechanical breaking in ultra-high vacuum (UHV). More recently, they have been obtained by electrochemical etching of cylindrical rods in NaOH solution [10]. Both these methods lead to tips with a good aspect ratio. Only in Refs. 8, 9 it has been shown that Cr tips can achieve atomic resolution on the Si(111)-7×7 reconstructed surface, while SP-STM measurements are not reported. It must be observed that both procedures contain some delicate and complex steps: either breaking an etched rod in UHV in one case, or shaping the rod to cylindrical section in the other. These aspects could make the realization of Cr tips rather complicated. We developed a simplified procedure which avoids the above mentioned steps. We started from rods of polycrystalline Cr with a nearly square cross section of 0.7 mm × 0.7 mm obtained by cutting a 99.99 % Cr foil. Asymmetrical shape of the rods due to lack of uniformity in the foil thickness can often result in a bad aspect ratio, nevertheless atomic resolution on atomically flat surfaces could be easily achieved anyway, as described below. The etching procedure can be divided in two steps; in the first, we perform a pre-etching, with a ring-shaped gold cathode, applying a DC voltage in the 5-7 V range in order to reduce the rod cross-section, while in the second step etching is performed using a DC voltage in the 3-4 V range. Both NaOH and KOH 1.5 M solutions have been tested with good results. During the etching we observe formation of Na/K and Cr compounds on the surface of the rod. These compounds are soluble in water and can be removed by stopping the pre-etching and washing the rod in a water ultrasonic bath. A lower voltage is used in the second step to limit the accumulation of the compounds on the rod. SEM images of the various Cr tips obtained after the described procedure have been acquired (not shown). In general, we observed that even though the overall shape on a micron scale is usually far from being regular, the tip apex is sharp at least at the observed scale (tens nm).

RT, constant current STM measurements with Cr tips have been performed using a Omicron UHV VT-SPM. The tips were tested on the Au(111) surface, as a typical example of a metallic system. In Fig. 1 a topographic image of this surface is shown. It can be observed that

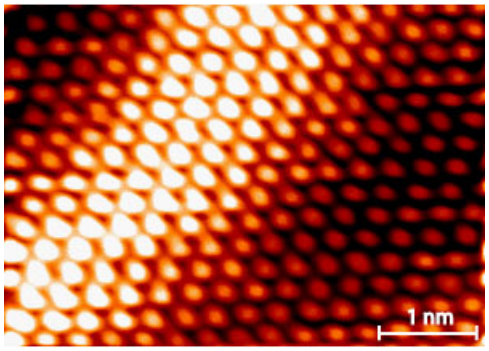

FIG. 1: Image of Au(111) surface taken at V_b=1 V, I_b=1 nA and at T=300 K, showing superstructure and atomic resolution.

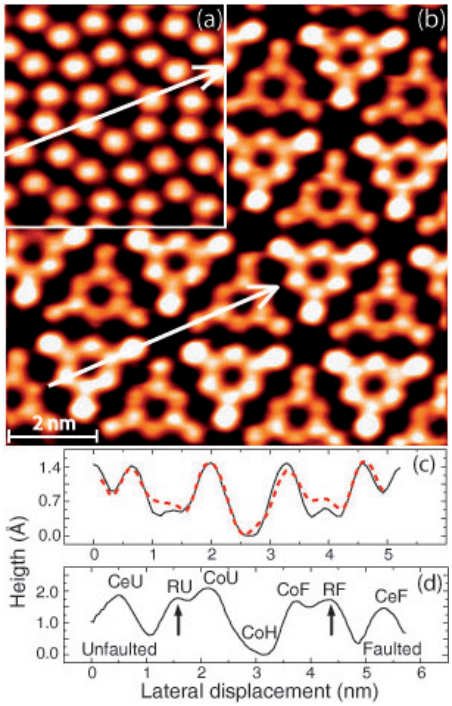

FIG. 2: Images of Si(111)-7×7 surface taken at (a) V_b=1 V and I_b=1 nA and (b) V_b=-1.5 V and I_b=2.2 nA. The presence of rest atoms (R) can be observed between the corner (Co) and the two center adatoms (Ce), in both faulted (F) and unfaulted (U) half (CoH indicates the corner hole of the cell). (c) Line profile along the diagonal of the cell of case (a), taken with a Cr tip (black solid line), vs. normalized line profile taken with a W tip at V_b=1 V (red dashed line). (d) Line profile along the diagonal of the cell of case (b).

atomic resolution, clear separation among atoms as well as the characteristic superstructure are easily achieved.

The Si(111)-7×7 surface was chosen as the main test surface. It is a very well known surface, both theoretically and experimentally. It is also one of the most investigated surfaces with STM (see e.g. Ref. 13 and references therein). The complex structure of its 7×7 unit cell [14] makes it ideal in order to test the capability of resolving detailed energetic and spatial features with sub-nm resolution. It is well known that, with commonly used tips, at positive applied bias the topographic STM image clearly shows the twelve adatoms [15], while at negative bias the corrugation amplitude is worse. In usual conditions rest atoms, which lie about 0.7 Å below the nearest corner adatom, are not observed: they have been detected using particular semiconducting tips, able to suppress the signal from the adatoms [16]. In a recent paper [17], the rest atoms have been imaged using W tips with exceptionally high aspect ratio: they have been resolved only at the bias of -1.5 V and a net distinction from the corner adatoms is evident only in the unfaulted half. In Fig. 2(a) we report a representative image of the Si(111)-7×7 surface at +1 V bias obtained using a Cr bulk tip, where excellent separation between adatoms can be appreciated. In Fig. 2(b) the same surface is then shown at -1.5 V. One can clearly observe the distinction between faulted and unfaulted half cell, the net separation between different cells and, above all, the presence of all the rest atoms belonging to the unit cell. Line profiles, like the one shown in Fig. 2(d), allow distinguishing rest atoms both in the unfaulted and faulted half of the cell. While Wang et al. [17] claimed that rest atoms could be observed only with two of the many W tips used, here, using bulk Cr tips, we observed rest atoms routinely, with all the tips we used. This is a first important evidence that Cr bulk tips allow for a peculiar sensitivity, reducing convolution effects of the tip and enhancing its capability of resolving details in the observed topographic and electronic structure.

A different tip sensitivity can be ascribed both/either to its geometrical configuration (local curvature radius, aspect ratio) and/or to its local electronic density of states (LDOS) properties and to the spatial distribution of the apex atom electronic orbitals. In the work by Wang et al. a simple model of the surface line profile as a function of the tip curvature radius is discussed, observing that it is necessary to use a tip with an equivalent radius of about 7 Å in order to distinguish at least the rest atom of the faulted half. Since our result was obtained for all the Cr tips used, it may be not sufficient to explain it only in terms of a very sharp geometrical shape of the apex, because such a control and reproducibility of the final tip curvature radius and aspect ratio appears beyond the possibilities of our simplified fabrication method. Therefore, electronic properties and in particular the local density of states at the Cr tip last atom, which is reasonably nearly the same in all the tips, could be the factor that mostly contributes to the peculiar properties observed.

As a further investigation, we compared performances of Cr bulk tips with home-made W tips obtained with a standard etching procedure [1]. Line profiles of the same Si (111)-7×7 surface obtained with Cr and W tips, both at V_b=1 V and I_b=0.5 nA, are compared in Fig. 2(c). We evaluated the line profiles of these images along a cell diagonal and we normalized them so that the max-

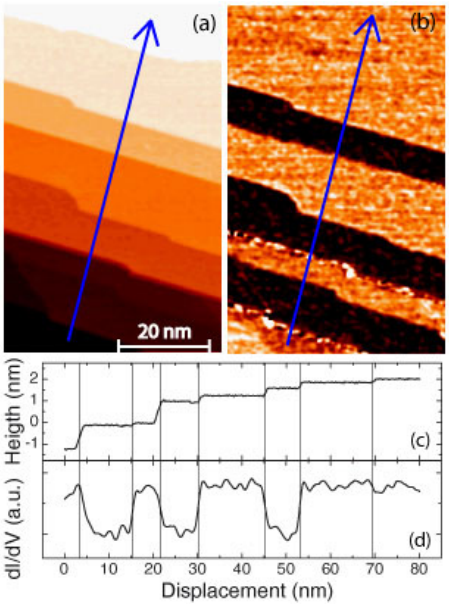

FIG. 3: (a) Topographic and (b) differential conductivity maps of Cr (001) surface taken at V_b=-0.37 V and I_b=1 nA. Line profiles (c) and (d) clearly show the magnetic contrast obtained with Cr bulk tip. The image contrast of the differential conductivity map is $\sim$ 15 % while the signal-to-noise ratio is $\sim$ 4.

imum height excursion (corresponding to the excursion between the corner adatom and the corner hole) is the same for the W and the Cr tip. By doing so we want to compare the imaging contrast and resolution of the tips, normalizing for effects related to different barrier heights and different tip-to-sample distance. It can be noted that there are no significant differences both in the height contrast and in the lateral atomic resolution. This again supports the conclusion that the observation of rest atoms at -1.5 V bias is probably related to the Cr apex electronic structure rather than to a geometrical factor.

All these results provide strong arguments towards the interest in the performances of bulk Cr STM tips. If combined with the anti-ferromagnetic properties of Cr, SP-STM and scanning tunneling spectroscopy (STS) experiments exploiting the advantages of an elemental bulk tip with enhanced sensitivity are foreseen. We performed preliminary SP-STM measurements with these tips choosing one of the most investigated magnetic surfaces via SP-STM/STS techniques, namely the Cr(001) surface. It is well known that in this system terraces with opposite magnetic in-plane polarization can exist [18] and can be directly observed performing SP-STM/STS measurements [19]. In Fig. 3 we show a topographic image taken at V_b=−0.37 V (a) and a differential conductivity map (b) acquired at the same bias with our bulk Cr tip. The corresponding line profiles are also shown. Even if a direct quantitative comparison with previously reported data on clean Cr(001) is not possibile because of the presence of contaminants on our sample [20], nevertheless the capability of resolving the magnetic contrast is clearly evident. Therefore, bulk Cr tips exhibit in-plane magnetic sensitivity, leading to the possibility of achieving SP-STM with them.

In conclusion, we have presented a simplified method to produce Cr bulk tips and an investigation of their potentiality as STM probes. Lateral sensitivity of these tips, probably due to the features of the tip LDOS structure, can significantly enhance the quality of the STM image of an atomically flat surface. Atomic resolution on Si(111)7×7 has been easily achieved and rest atoms of the Si (111)-7×7 reconstruction have been routinely resolved. Successful tests on the magnetic Cr(001) surface have been conducted, demonstrating the feasibility of performing SP-STM measurements. We believe that this work opens the way for a useful introduction of this kind of STM probes in (SP-)STM/STS experiments, which allows avoiding either in-situ evaporation or use of non elemental materials for tip preparations.

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